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(54) Title: HIGH TEMPERATURE PASSIVATION OF RARE EARTH MAGNETS			
(57) Abstract A rare earth based permanent magnet having a corrosion resistant surface comprising a magnetic body having an external surface formed from at least one rare earth metal alloy and a high temperature passivated layer substantially surrounding the external surface of the magnetic body. A method for passivating a neodymium based rare earth magnet through high temperature thermal conditioning in a controlled atmosphere environment.			

HIGH TEMPERATURE PASSIVATION OF RARE EARTH MAGNETS

FIELD OF THE INVENTION

5 The present invention relates to permanent magnets manufactured from rare earth elements having corrosion resistant surfaces and a method for the preparation thereof. More particularly, the invention relates to permanent magnets formed from alloys primarily comprising neodymium, iron and boron, which are formed with a high temperature passivating film that is highly resistant to corrosion and oxidation.

BACKGROUND OF THE INVENTION

10 Many conventional rare earth magnets are composed of metal alloys and mixtures that are well known in the art and the literature. Rare earth magnets generally contain various percentages of at least one rare earth element from the lanthanides group of elements. Other components
15 include non-rare earth elements such as iron, cobalt, nickel and boron. All of these commonly used magnetic ingredients may be formed into alloys or mixtures containing one or more rare earth elements that are generally known to exhibit good magnetic properties.

20 Rare earth magnets are often described and identified according to their relative compositions of rare earth elements and other constituents. For example, commonly preferred types of rare earth magnets contain alloys of neodymium or praseodymium in combination with iron and boron. These magnetic alloys may further include a wide range of other elements such as aluminum, gallium, copper, iron, zirconium, titanium, cobalt, carbon, palladium, uranium and the like. Other rare earth magnets may be formed from alloys of samarium, cobalt and iron. Still other rare earth magnets may include alloys containing appropriate proportions of dysprosium

and cobalt, and other suitable magnetic materials.

A common problem with rare earth magnets or magnetic materials is that they are readily oxidized and eventually corrode. This undesirable effect reduces the magnetic retentive capacity of the magnets, and is particularly significant at elevated temperatures above approximately 125-
5 150°C. The use of such reactive rare earth elements in these magnets frequently limits their application to surrounding temperatures under 100°C. It is also known that rare earth magnets, especially in their basic powdered form, are highly reactive when exposed to oxygen, moisture, salt-containing environments, and chemical agents containing chloride ions. The rare earth elements react similarly in these conditions as members of the same chemical group. Although
10 rare earth magnets are well known, and their extensive applications greatly realized, there exists a continuous need to improve their resistance to oxidation and corrosion stability when exposed to various operating environments. For this reason, it has been proposed to provide an oxidation-resistant protective layer on the surfaces of rare earth magnets.

A wide variety of protective layers for rare earth magnets may be formed from many
15 conventional materials including oxidation resistant compositions and mixtures, or corrosion inhibitors that passivate or substantially abate the reactivity of magnets. It is generally understood and acknowledged that a binding reaction occurs between the oxidation resistant composition or the corrosion inhibitor with the surface of the rare earth magnet. As a result of this surface interaction, the oxidation resistant composition or corrosion inhibitor is attached or
20 adhered to the surface of the particle in the form of a protective layer or coating. These coatings substantially encapsulate or surround the magnetic bodies, and to some degree, partially neutralize the reactivity of their magnetic constituents. In general, these types of passivating agents are added and mixed with the magnetic material during processing. Basic magnetic material often exists in the form of larger particles that are reduced in size through grinding or

other conventional methods. An effective amount of the oxidation resistant composition and/or corrosion inhibitor may be immediately added upon breaking or shearing of the magnet particles. These passivating agents have been found to generally render inert the otherwise exposed surfaces of magnetic particles or aggregations thereof. Before any considerable oxidation can occur, the passivating material is applied to minimize or immediately arrest corrosion.

Rare earth magnets and magnetic materials may also be formed into larger sized magnets by a process known as sintering. In the presence of suitable levels of heat and pressure, particles of a rare earth magnet or magnet material may be sintered through standard techniques into a much larger article with the desired density and configuration for an end use product. The addition of passivating agents, or other suitable antidegradant agents, may be applied to the surface of the sintered rare earth article in any conventional manner such as by spraying, brushing or dipping. Various configurations for the protected magnetic material may be achieved that are suitable for use in a wide variety of electromechanical devices including motors, coils, actuators, etc. Magnetic articles may also be formed by mixing the rare earth magnet or magnetic materials with binder agents that assist in forming the magnetic bodies into a desired configuration.

Permanent rare earth magnets consisting of neodymium, iron and boron, hereinafter referred to as the NdFeB magnets, have several distinct advantages over other rare earth magnets that may be based on samarium or cobalt. NdFeB magnets generally provide a high degree of magnetic performance and exhibit magnetic properties that are often far better than those of conventional samarium or cobalt based rare earth permanent magnets. It has been observed that less neodymium is required for rare earth magnets as compared to these other conventional permanent magnets. Neodymium is also naturally more abundant than samarium, and is available in sufficient quantities as a substantial magnet constituent. Rare earth permanent

magnets containing neodymium as a rare earth element are especially favored, and are continuously replacing the samarium or cobalt based rare earth permanent magnets in relatively smaller types of magnetic circuits. The economical advantages of shifting to neodymium based rare earth magnets has even motivated their use in various applications that previously relied upon less effective ferrite materials or costly electromagnets. As a result, the demand for NdFeB magnets has rapidly grown, along with their expansion in applications, as high performance magnets in many common devices such as electric motors, actuators and sensors. Because of their excellent magnetic properties and relatively low cost, these types of magnets are also used extensively in the electric and electronic industrial fields, particularly in electrical parts for the automobile industry. The constantly progressing technology in these fields demands further improvements in the performance of these magnets.

However, like all of the other rare earth elements, the basic disadvantage of NdFeB magnets is their high chemical activity as an alloy which adversely affects all stages of production. Its reactivity is particularly noticeable during fine milling and caking processes. This is partially due to the fact that rare earth metals possess a relatively high standard electrode potential (E₂₉₈). For all the rare earth metals, this value (E₂₉₈) ranges from approximately -2.25 to -2.52. Higher potentials are generally observed only with alkaline metals or Group IA elements. The intergranular phase of NdFeB magnets is enriched with neodymium which has a standard electrode potential (E₂₉₈) value relatively higher than its other alloying metals (E₂₉₈ = 0.913B (Cr), -0.44B (Fe), -0.25 (Ni)). As a result, NdFeB magnets are highly sensitive to electrochemical corrosion. Neodymium alone has an unfavorable tendency to also easily oxidize in air, and particularly, in moist air. This oxidation not only gives rise to the formation of an oxide layer on the surfaces of the magnet, but it also proceeds inwardly into the magnetic body to cause intergranular corrosion which typically develops along the grain boundary of the

alloy. This phenomenon is the most noticeable in the neodymium based magnets because of the very active neodymium enriched phase that often exists in the grain boundary of these structures. During this electrochemically corrosive process, the function of the cathode is performed by grains of the main magnetic phase of the alloy, $\text{Nd}_2\text{Fe}_{14}\text{B}$. The anodic function is performed by the intergranular neodymium enriched phase of the alloy and the isolates of the NdFe_4B_4 phase. The amount of NdFe_4B_4 phase alloy in conventional commercial magnets typically ranges from approximately 80 to 85% in volume. The relative proportions of Nd_2O_3 is approximately 1-5% in volume, and that of the $\text{Nd Fe}_4 \text{ B}_4$ phase may be up to 8% in volume. The remaining composition of the alloy mainly consists of the neodymium enriched intergranular phase alloy. The relatively small amount of anode phase alloy is an especially negative factor with respect to electrochemical corrosion since a considerable amount of current must pass through these small phases that further worsens the extent of corrosion. This type of intergranular corrosion leads to a profound decrease in magnetic properties of the structure, and if the corrosion progresses while the magnet is in use, the performance of the apparatus using the magnet deteriorates and eventually leads to its failure.

The problem with corrosion in rare earth magnets is further aggravated by the multitude of pores and microcracks appearing on the magnet surfaces that result from current methods of magnet powder manufacture. It has been observed that pores and cracks sharply intensify electrochemical corrosion. This is partially due to a high capillary condensation of water vapors in the pores that undesirably attracts moisture. In addition, the electrolyte composition in relatively small pores may change such as when the concentration of chlorine and hydrogen ions increases to stimulate the corrosive dissolution of the magnetic material. Metallic materials and their processed end products are chemically active and are typically formed with nonuniform surfaces that promote corrosion. These disadvantages associated with rare earth magnets pose

many problems in their processing and limit their range of potential applications. For example, with respect to permanent rare earth magnets containing iron or cobalt, their exposed surfaces easily rust because the magnetic material is readily oxidized in ordinary operating environments. The formation of the resultant oxide on the magnet surfaces degrades the output of the magnetic circuit and impinges upon its performance. The oxide also has a fairly loose structure and sheds from the magnet surface thereby smearing other devices disposed nearby. The resulting oxidation and corrosion presents various problems that only proliferate over time.

In light of these very serious drawbacks with using NdFeB magnets, which include their lack of resistance to corrosion or oxidation as with most rare earth magnets, there is a continuous need to develop a highly corrosive resistant NdFeB magnet. Various attempts have been made in the past that provide only limited results, and often involve relatively complicated procedures. Several methods have been proposed for improving the corrosion resistance of NdFeB magnets including the formation of a protective film by electrolytic or electroless nickel plating, or aluminum-ion chromating. Other proposed techniques for providing metallic articles with corrosion proof or rust proof layers include the spray coating or application of various epoxy resins.

A conventional method for protecting active metals involves the application of chemically stable galvanic coatings of transition metal elements such as nickel, zinc, chromium, or other suitable protective elements. Application of these protective coatings, however, often presents severe disadvantages that weigh against their utility. For example, many problems arise when attempting to form coatings of metals such as zinc over magnetic bodies. The devices used to form these types of coatings are often complicated and bulky. The method itself is also deficient in operational efficiency, incapable of mass-production, and a relatively expensive process. While the addition of these coatings may be effective in improving resistance to

corrosion, they are also often detrimental to the magnetic properties of rare earth magnets, including NdFeB magnets, and tends to dilute their strength. The relative amounts of these protective materials surrounding a magnetic article is therefore limited to a very small quantity. As a consequence, the advantages offered by the addition of this layer for protection against corrosion are often not justified.

The inherent pores and cracks in NdFeB magnets also complicate the process of applying galvanic coatings to their surfaces. Common types of protective layers for these rare earth magnets include an electroplated nickel layer, an aluminum ion-plated layer, or films formed of other suitable material. The process of nickel electroplating is advantageous in that the resulting surface protective layer is excellent in mechanical strength, and the layer will not in itself appreciably absorb humidity. However, it is difficult to form protective layers of uniform thickness by nickel electroplating. The plating current tends to concentrate on outer peripheral portions of irregular surfaces since it is difficult for the plating current to pass through inner holes and inner peripheral portions. Magnets having peculiar shapes, such as a cylindrical magnet, often have inner peripheral portions that are hardly coated with the electroplated nickel layer. As a result, the film thickness becomes relatively thin in these regions and a sufficient degree of uniformity in the film thickness cannot be achieved by nickel electroplating alone.

Furthermore, coatings derived from materials such as phosphate or chromate may deteriorate the physical properties of substrate metals and diminish their metallic properties. Other relatively complicated procedures, which include vapor plating methods, vacuum deposition, ion sputtering, and ion plating, are also costly and are often not effective in coating surfaces of magnetic bodies that are formed with irregularities such as holes, cracks and grooves. In addition, because all known metal coatings are generally cathodic due to their relatively lower standard electrode potential values (E298) in comparison to rare earth metals, any disturbance in

the coating continuity (e.g., micropores) may intensify the process of corrosion as compared to a noncoated magnet. This typically leads to complete deterioration of the protective coating and may interfere with the performance of the magnet and its host apparatus. For example, when a NdFeB magnet is provided with metal plating, its corrosion resistance greatly depends on the surface condition of the magnet body. Its resistance to corrosion is severely decreased when an oxidized or degraded layer is already formed on the magnet surface which has poor magnetic properties, or is formed with pores or any other type of surface irregularity. Permanent magnets formed with the aforementioned corrosion proof coatings provide limited effectiveness in resisting corrosion. The passivation of magnetic surfaces by these involved and complicated methods therefore involve the addition of a non-magnetic layer, the possible deterioration of magnetic properties, and the needless etching or otherwise altering of magnetic body surfaces which may weaken the overall strength of the magnet.

It has been proposed to alternatively provide the surface of rare earth magnets with a surface coating of suitable non-metallic materials that are corrosion resistant. According to the concepts of presently accepted passivating methods, these oxidation resistant compositions may include epoxy silanes and/or an epoxy resin compound. Forming resinous coatings generally requires a relatively large layer thickness because the applied layer of resin often has a particularly porous texture. The thick coating of resin consequently formed may also hinder the application for which the coated article is intended. For example, when the magnet is used as a rotor magnet for a motor, the motor would tend to have an undesirable large air gap between the coated rotor magnet and the stator which significantly reduces the potential torque capacity of a motor. Moreover, when magnet surfaces are coated by spraying or electrocoating with such a resin film, this often results in rusting immediately beneath the film due to the hygroscopicity of the resin. The resulting protective layer absorbs an appreciable amount of moisture or humidity,

and exhibits relatively poor mechanical strength. Although these methods may be used in several particular applications and are in some way practicable, they often fail to provide adequate protection and satisfactory results. The adhesion of these films therefore provides only limited success in improving the corrosion resistance of rare earth magnets thereby demanding further improvements in the field.

Numerous other methods have been proposed to protect rare earth magnets against corrosion. Many metals may be protected against electrochemical corrosion, for example, by coating their surface with a protective oxide film. A classic example of this type of procedure is the formation of a passivating film of Al_2O_3 on the surface of aluminum. These passivating films ensure good performance when they are not excessively thick, which presents fewer surface defects in the protective layer, and adhere intimately to the protected substrate metal. Most preferably, the passivating films are epitaxial or do not form distinct boundary layers. The oxides initially produced on the exposed surfaces of magnetic materials, however, generally include a loose, and often amorphous, structure that does not arrest the process of oxidation. There have also been previously failed attempts to chemically treat magnetic surfaces with various reagents to improve their resistance to corrosion. For example, when magnets were chemically treated with particular solutions, their resistance to oxidation and corrosion may be actually hindered. It was found that a majority of chemical solutions often worsen the corrosion resistance of magnets. Accordingly, many technical and complicated solutions have been developed with mixed results concerning the corrosion resistance of NdFeB magnets and other rare earth magnets.

SUMMARY OF THE INVENTION

The present invention provides rare earth magnets with corrosive resistant films that are

formed through high temperature thermal treatment. The methods disclosed for producing high temperature passivating films may be conducted in a vacuum environment. Except as specifically described herein, the equipment used for application of these high temperature passivating films are that of a standard design ordinarily used in the manufacture of magnets.

5 Of course, the present invention may be carried out in other suitable equipment that achieves the conditions and intended goals with rare earth magnets as described herein.

The treatment process itself is sufficiently efficient and productive to be carried out on a relatively large scale. The present invention is directed to the passivation of rare earth magnets in order to greatly reduce their tendency to corrode without adversely affecting their magnetic

10 properties, and their structural and chemical integrity. In one embodiment of the present invention, the rare earth magnet is formed with a passivating layer when subjected to high temperature thermal treatment and regulated pressure. The corrosion resistance of NdFeB magnets may be increased by the disclosed methods of high temperature passivation in a vacuum environment where the passivated layer formed on magnets may range from approximately 10 to

15 30 microns in thickness. The thickness of the passivated layer may vary beyond this particular range. Rare earth magnets formed with varying thicknesses of this passivated layer achieve protection against corrosion in accordance with the present invention.

Another variation of the present invention includes a method of forming a corrosion resistant passivating layer on the surface of NdFeB magnets by high temperature thermal

20 processing in a controlled environment. The process of forming these protective films presents no stringent requirements as to the surface quality of magnets. Magnets manufactured with existing cleavages and microcracks are permissible, and demonstrate a high resistance to corrosion upon treatment according to disclosed methods. This flexible method of passivating rare earth magnets such as NdFeB magnets is also directed to avoiding complicated inspection

procedures for selecting suitable magnets, and limiting the percentage of rejected magnets. These methods of high temperature passivation do not place strict requirements for a high finish surface on the magnet bodies. The passivating film may be readily formed on nonuniform surfaces having cleavages, cracks or other deformities.

5 In yet another embodiment of the present invention, passivating films are formed onto surfaces of rare earth magnets that do not worsen their magnetic and structural properties. The magnetic characteristics of the formed structure remain intact after passivation, and there is no separation of soft magnetic phases in the material. Application of passivating films by the disclosed methods of high temperature passivation produces no adverse effect on the magnetic
10 characteristics of the structure. The passivating layer may consist of oxides derived from various rare earth metals and other alloying elements present in the magnet. The protective film adheres strongly to the magnet surface and stands well against various mechanical effects such as scratching without detriment to its protective properties against corrosion and oxidation.

Another variation of the present process includes the formation of a high temperature
15 passivating layer that arrests the process of corrosion and prevents its proliferation. If corrosion centers develop on the rare earth magnet, the corrosion process still does not take on an avalanche-like nature as with other coatings. The formation of any corrosive products does not include coarse or loosely dispersed particles or contaminants. Pursuant to these disclosed methods, corrosion is not permitted to spread over the entire surface of a magnetic body.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1(a) is a photograph of a magnet formed in accordance with the principles of the present invention generated by a scanning electron microscope (SEM) when viewed perpendicular relative to the high temperature passivated surface.

FIG. 1(b) is a photo micrograph of another magnet formed in accordance with the principles of the present invention generated by a scanning electron microscope (SEM) when viewed perpendicular relative to the high temperature passivated surface.

FIG. 2 is a graphical description of temperature and pressure variations during another sample heat passivation process described in this embodiment of the invention.

FIG. 3 is a graphical description of the temperature and pressure variations during a sample heat passivation process described in this embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The concepts of the present invention may be applied to rare earth magnets generally regardless of their chemical composition or geometrical shape. The proceeding results and analysis, however, were obtained with circular radial texture NdFeB magnets having an overall height, length and width dimension measuring 23.88 cm x 19.82 cm x 5.53 cm, respectively. The concepts of the present invention may of course be evenly applied to other rare earth magnets with varying dimensions and configurations. The magnets described herein were manufactured according to a wet forming method, including milling in a C₂H₅OH medium, within the established framework of accepted integral processes for the magnets. The magnets were basically divided into two groups differing in alloy composition, charge materials and manufacturing methods.

Group A

Alloy composition :

33.5%Nd- 1.0%Dy- 2.5%Co- 0.8%Al- 1.0%Ti- 1.15-1.25%B-0.025%U-U% Fe.

The alloy was melted with metallic neodymium.

Group B

Alloy composition:

33.6%Nd- 1.35%Dy- 0.4%Al- 0.78%Ti- 1.17%B- 2%Co-0.025%-U% Fe.

Group B magnets were made from the base alloy (65%) with additions of dysprosium, neodymium and boron. Metallic neodymium was used for melting the base alloy only. The
5 additions were melted from the charge of an approximate composition based on the alloy 30%Nd-1%B-Fe.

In accordance with the principles of the present invention, a chemically homogeneous film may be produced on the magnet surface by high temperature passivation in a vacuum environment. Elevated temperatures are generally known to promote the occurrence of diffusive
10 processes. The homogeneous passivating film may be formed by ensuring a dynamic equilibrium between the reactions of formation and the reactions of decomposition of the passivating film. These competing reactions are controlled by selecting appropriate conditions including preferable temperatures, surrounding pressure and time of exposure. High temperature
passivation of the NdFeB test magnets were carried out in standard electric vacuum resistance
15 furnaces such as a CHB3 type apparatus that is typically used for baking and heat treatment applications. The basic process for high temperature passivation of these magnets may consist of heat treatment at a temperature of approximately 1000°C for about 30 minutes in a vacuum environment where the surrounding pressure ranges from approximately 1.0×10^{-5} to 1.0×10^{-6} mm Hg. It should be noted that these selected values were the particular maximum limit for the
20 furnace used in the passivating process, and does not in any way restrict the scope of the present invention which may achieve a higher temperature passivated layer beyond these particular temperature or pressure values. As with most forms of heat treatment, the surfaces of magnets were prepared in advance by degreasing and chemical pickling. Having selected preferable methods of surface preparation, the accompanying conditions of high temperature passivation

were varied which included changing the temperature, time of exposure, and surrounding pressure. It was observed that 1000°C was the maximum temperature at which there was practically no shrinkage of the magnets or change in their geometry. Additionally, the heat treatment of the NdFeB magnets at this range of temperatures for Groups A and B alloys may provide additional intensification of their magnetic characteristics.

The resistance of the NdFeB magnets studied were subjected to various forms of accelerated testing methods. In general, the method of accelerated testing used with the present invention did not change the corrosion mechanism of magnets that is encountered in actual service. These methods comply with the typical working modes for NdFeB magnets, and are relatively simple to reproduce for purposes of testing. For example, the magnets intended for service in a relatively humid climate should be tested in the presence of NaCl, while the simulation of an industrial environment should include SO₂ which is a common contaminant in that type of surrounding. It is further known that the presence of NaCl speeds up anodic reactions since Cl⁻ ions aggravate the decomposition of existing passivating films. It should be noted that tests at elevated temperatures are not always effective in measuring resistance against corrosion since the water solubility of oxygen at temperatures exceeding 60°C often drops sharply. As a result, this delays the processes associated with oxygen depolarization and does not provide a true indication of corrosion resistance. A preferable method of accelerated testing involves soaking magnet specimens in an aqueous solution of NaCl at a concentration of approximately 3% by weight at room temperature. The stability criterion for passivating films include the time of emergence, and the number and nature of corrosion centers.

In many instances, the corrosion stability of metals are assessed by changes in the weight of selected specimens. Depending on the particular method of measurement selected, the recorded change in weight may be increased or reduced. It has been observed that

electrochemical corrosion is substantially influenced by both the process factors, i.e. surface finish, porosity, etc., and by the specific composition of the material. For example, an increase in the neodymium component of an alloy from 34% to 37% by weight may reduce its corrosion rate by approximately one half. This has been observed under varied test conditions where the surrounding temperature was 150°C or 20°C, the relative humidity was 15% or 95%, and the surrounding pressure was approximately 5 psi. The rate of corrosion may also be affected by varying the composition of the alloy to include small additions of elements such as iron, chromium, titanium, zirconium and lead. During various methods of accelerated test conditions, which include acid corrosion, atmospheric corrosion and salt fog tests, the addition of chromium produced the best effect in minimizing electrochemical corrosion. For example, during salt fog tests, the typical weight change of a specimen after 10 hours of soaking was about one and a half times lower than samples containing titanium. It should be noted that the rate of electrochemical corrosion in these conditions was assessed by the changes in weight of the test magnets. Accordingly, many alloying combinations promote the improvement of their relative resistance to corrosion, which continues nonetheless, but at different rates with varying compositions. Regardless of the type of surface treatment, electrochemical corrosion continues and is constantly present since alloying constituents inherently tend to form voltaic couples. The chemical and structural nonhomogeneity of these magnet materials unavoidably leads to electrochemical corrosion.

The results of the corrosion resistance tests for the NdFeB magnets are provided in Table 1. The method of accelerated testing used involved soaking the magnet specimens in an aqueous solution of NaCL at a concentration of approximately 3% by weight at room temperature. Corrosion resistance was measured at the time, t_{50} , that 50% of the sample surface was corroded.

16

TABLE 1

No.	Pressure (torr)	Temperature (°C)	Time (minutes)	Oxygen Content in atmosphere (volume %)	t ₅₀ (hour)
1	5 x 10 ⁻¹	1000	12	21	130
2	10 ⁻¹	1000	20	21	490
3	10 ⁻²	1000	40	21	>>10000
4	10 ⁻³	1000	60	21	>>10000
5	10 ⁻⁵	1000	120	21	6000
6	10 ⁻⁶	1000	240	21	520
7	5 x 10 ⁻⁶	1000	249	21	120
8	10 ⁻²	700	50	21	180
9	10 ⁻²	800	40	21	920
10	10 ⁻³	1000	60	21	>>10000
11	0.5 x 10 ⁻⁴	1100	40	21	170
12	5 x 10 ⁻⁴	1120	10	21	30
13	5 x 10 ⁻³	1050	5	21	48
14	5 x 10 ⁻³	1050	10	21	190
15	5 x 10 ⁻³	1000	60	21	>>10000
16	6 x 10 ⁻³	1000	240	21	1300
17	6 x 10 ⁻³	1000	300	21	870
18	9 x 10 ⁻²	1000	230	0.0001	350
19	9 x 10 ⁻²	1000	200	0.001	3100
20	10 ⁻²	1000	60	10	>>10000
21	10 ⁻³	1000	60	21	>>10000
22	5 x 10 ⁻⁴	1000	30	40	780

In accordance with another variation of the present invention, the surfaces of rare earth magnets may be preliminarily prepared for improved high temperature passivation. Since the surface of magnets after grinding is often soiled with grinding waste, products of interaction with the cutting fluid, etc., the magnets are preferably degreased in advance by rinsing them in organic solvents such as freon or acetone. Next, the surface may be cleaned by pickling techniques in aqueous solutions of suitable acids including HNO₃, H₃PO₄ and HF. The concentration of

these acids preferably range from approximately 0.6, 1.25, 2.5, 5.0, 10.0, or 100 percent by volume. The pickling time preferably ranged from about 0.5 to 25 minutes. During testing, some control specimens were tested without pickling. It should be noted that the pickling of magnets without high temperature passivation gives virtually no effect to its resistance to corrosion. A preferable method of surface preparation involves pickling in a 2.5% solution of H_3PO_4 for about 2 minutes. The positive effect of pickling may be due to the increased homogeneity of the magnetic surface. For example, the results of investigations of group A magnets on the SUPERPROBE-733 apparatus before and after pickling in 2.5% solutions of either H_3PO_4 or HNO_3 (for about 2 minutes) demonstrated that the size and number of surface pores diminished successively while shifting from the unpickled specimen to that of a pickled sample in solutions of either HNO_3 or H_3PO_4 . It has been observed that if the maximum size of pores in the initial unpickled specimen reach 100 microns, they are not over 30 microns when pickled in a H_3PO_4 solution. The reduction of the number of surface pores, while all other conditions being equal, contributes to the high homogeneity of the passivating film which significantly reduces the effects of electrochemical corrosion. It should be pointed out that pickling did not significantly decrease the magnetic characteristics of the specimens. In fact, the sum of maximum absolute magnetic field values on the Hz axis of an initial magnet was 73.6 mT, while after pickling in a 2.5% solution of H_3PO_4 for 15 minutes, it changed to only Hz = 73.2 mT.

20 In determining preferable operating conditions for carrying out the present invention, selected ranges of surrounding temperature and pressure were evaluated to determine their impact on the high temperature passivation of rare earth magnets. While practicing the conditions of high temperature passivation on NdFeB magnets, the range of temperatures tested with this heat treatment ranged from approximately 500°C to 1100°C. The surrounding pressure

during testing ranged from approximately 1.0×10^{-4} to 1.0×10^{-6} mm Hg. The time of exposure for the specimens at these conditions and the selected high temperatures ranged from about 10 to 120 minutes. The specimens were then removed after the heat treatment process and exposed to air and ambient conditions. Figure 2 is a graphical description of temperature and pressure variations during a sample heat passivation process described in this embodiment of the invention.

In accordance with another variation of the present invention the surrounding pressure during heat passivation is controlled in two phases. During the first phase, the surrounding pressure ranged from approximately 1.0×10^{-4} to 1.0×10^{-6} mm Hg. The range of temperatures for this heat treatment ranged from approximately 500°C to 1100°C . The time of exposure for the specimens at these pressure and temperature conditions ranged from about 10 to 120 minutes.

During the second phase, the surrounding pressure ranged from approximately 1.0×10^{-2} to 1.0×10^{-4} mm Hg, while the temperature remained in the range of approximately 500°C to 1100°C . The time of exposure for the specimens during the second phase ranged from 10 to 120 minutes. Thereafter, the specimens were permitted to cool with under vacuum conditions where the surrounding pressure was varied between approximately 1.0×10^{-4} to 1.0×10^{-6} mm Hg. The duration of the cooling process ranged from 5 to 30 minutes. The specimens were then removed and exposed to air and ambient conditions. Figure 3 is a graphical description of the temperature and pressure variations during a sample heat passivation process described in this embodiment of the invention.

It must be noted that many additional parameters may be varied to facilitate passivation of the rare earth magnetic material that were studied. The results provided in the present disclosure represent only a sampling of possible conditions that may be controlled to assist high temperature passivation of rare earth magnets.

It was observed that preferable conditions for high temperature passivation occurred at a temperature of approximately 1000°C and at a pressure of approximately 8.0×10^{-4} to 9.0×10^{-4} mm Hg for about 30-120 minutes. For example, when heat treatment was performed in a helium environment at subatmospheric pressure, there were no positive indications of having passivated the sample. Similar results were also obtained when sample magnets were exposed to standard air and room conditions after being heat treated with temperatures ranging only from about 500°C to 600°C. After the magnet has been cooled, the microinhomogeneities (e.g., microcracks) of the protective layer can be filled by immersing the magnet into a polymer solution characterized by effective adhesive properties.

In accordance with the present invention, the high temperature passivation of rare earth magnets are performed in preferable heating and cooling conditions. The effects of high temperature passivation were observed at microsections of the magnet surfaces in photographs generated by a scanning electron microscope (SEM) that were taken perpendicular relative to the magnet coating surface. As illustrated in FIGS. 1(a) and 1(b), the passivating coating is clearly visible when viewed from the edge of the magnet body. It was observed that the coating thickness was approximately 30 microns in thickness for Group A magnets as shown in FIG. 1(a). As shown in FIG. 1(b), the thickness of the passivating layer was approximately 10 microns for Group B magnets.

A microscopic analysis of Group A magnets reveals that the basic components of the passivating coating are similar to the composition of the intergranular phase for the magnet. These results are summarized in TABLE 2. Upon further examination of FIGS. 1(a) and 1(b), it is apparent that the color of the intergranular phase and coating is also substantially the same. However, it was observed that the coating was not entirely chemically or structurally homogeneous. There appears to be distinct isolates of grey phase particles approximately 2

microns in size. The composition of these isolates also appears in TABLE 2. As can be observed from TABLE 2, the compositional analysis of each listed material does not cover all existing elements found in the specimens. The total percentage content for the intragranular magnet phase, light sections and grey isolates of the coating, were therefore less than 100 percent, and totaled only about 85.9, 86.5 and 83.3 percent, respectively. Some of the remaining elements most likely present, but not specifically included in TABLE 2, include light elements such as oxygen and boron. It must be noted that some of the irregularities observed on the external surfaces of the passivating films in FIGS. 1(a) and 1(b) were the product of certain conditions arising out of the preparation of the microsection, and have no bearing on the quality of the passivating coating. It was observed that the passivating films of Group A magnets, as shown in FIG. 1(a), revealed no noticeable traces of corrosion on their surface after soaking in a 3% solution of NaCl for a period of 14 days at ambient temperatures. Group B magnets were also observed to have a lower degree of protection relative to Group A magnets. This reduced resistance against corrosion may of course be simply attributed to the fact that the film on Group B magnets, as shown in FIG. 1(b), had a relatively smaller thickness (almost 3 times less). It should be noted that high temperature passivation, however, generally provides improved protection against corrosion not only to the smooth surfaces of magnets, but even with deep penetrating radial cracks formed in the magnetic bodies. While the corrosion center initially provides limited protection, in previously disclosed methods, the structural instability of this typical accumulation of oxides fails to arrest the debilitating process of corrosion from continuing throughout the magnet body. Regardless of the particular composition or structure of these types of corrosion products, they generally disperse along the magnet surface and impair the strength and structural integrity of the rare earth magnets. Unlike these previously known methods such as electrodeposition techniques, there are no stringent requirements for the

uniformity of the substrate surfaces when passivating rare earth magnets in accordance with the concepts of the present invention. Any corrosion centers that may develop also become localized and contained rather than spreading over the entire surface of the magnet.

TABLE 2

Results of SUPERPROBE-733 Microscopic Analysis
of Coating and Intergranular Phase of Group A Magnets

Composition of element, wt-%

<u>Element</u>	<u>Intergranular Phase of Magnet</u>	<u>Light Sections of Coating</u>	<u>Gray Isolates in Coating</u>
Nd	82.6	84.1	78.8
Fe	2.5	1.8	3.2
Co	0.43	0.11	0.17
Ti	0.001	0.0	0.004
Al	0.064	0.023	0.10
Si	0.008	0.088	0.0
Mg	0.35	0.21	0.0
Total	85.9	86.5	83.3

It is commonly known that there is a greater percentage of oxygen in rare earth magnets after their powder conversion processing from base material. With respect to NdFeB magnets, the amount of oxygen present may be so significant that it becomes comparable with that of boron. When ingots of NdFeB magnetic material contain 0.017 percent by weight of oxygen, the processed magnets may eventually contain as much as 0.63 percent by weight of oxygen.

Oxygen is observed to be predominantly present in the intergranular neodymium enriched phase of the rare earth alloy. It has been observed that the neodymium enriched phase consists of at least two phases of different composition and structure. One phase contains approximately 70 percent of neodymium and 15 percent of oxygen, respectively, by weight. If the composition of this phase may be expressed as an oxide with the formula Nd_2O_3 , the resultant ratio would be approximately 85.7 percent by weight of neodymium and 14.3 percent by weight of oxygen. It should be observed that the sum of weight percentages of elements in TABLE 2 for the intergranular and white phases of coating approaches very closely this value. Furthermore, when subjected to electrization with an electron beam source, additional data indirectly demonstrates that these phases are highly resistant. In accordance with the principles of the present invention, the high temperature passivating layer formed on the surfaces may therefore consist of a stable neodymium oxide that is apparently close in composition to Nd_2O_3 . Of course, as can be derived from TABLE 2, the passivating coating contains additional elements described above.

A possible formation mechanism for the passivating films is further detailed in the present disclosure. Generally, in most types of vacuum systems, the neodymium oxidation reaction (1) will be shifted sharply to the right:



This is partially attributed to the relatively high Gibbs potential (AG_T) for the reaction (1). At 1000°C , the Gibbs potential value AG_{1000} is $-343 \text{ kcal/g.mol K}$. Accordingly, the oxygen dissociation pressure in reaction may be readily determined in reaction (1) to be approximately equal to 1.0×10^{-38} atmosphere at equilibrium. However, there are no vacuum systems presently available that can attain such conditions. When a direct reaction occurs similar to reaction (1) that is thermodynamically possible, the neodymium oxide layer formed would still

only provide a relatively loose layer. If this formed oxide layer were to function as a passivating film, protection against electrochemical corrosion would be extremely ineffectual. Other thermodynamic possibilities may be assessed involving other reactions with the rare earth metals present in a magnet and oxygen. Additionally, the reactive properties of nitrogen may also be evaluated to determine its impact on the formation of the corrosion resistant passivating layer. This and other types of additional information may be obtained upon a complete microscopic analysis of the passivating coating in model experiments with controllable atmosphere of all magnet constituents including light elements.

In addition to this probable mechanism for the formation of high temperature passivating films, other factors may also be considered. Apparently, the positive effect of resistance to corrosion may be based on the chemical and the structural homogeneity of the magnet surface after high temperature passivation. As explained above, this type of coating consistency reduces the effect of electrochemical corrosion and contributes to its stability under various operating conditions. In the event there are minor inconsistencies in the thickness of the formed protective layer, the magnet surface may be further treated after high temperature passivation with a very thin layer or coating of varnish to mend these minor film defects. It has even been observed that the use of varnish on the magnet surfaces has made it possible to raise the stability of passivating films even further during autoclaving tests.

Another variation of the present invention includes the high temperature passivation of NdFeB magnets that are initially formed by caking methods to attain more than 90% of theoretical density. After the magnets are polished to required sizes, their surfaces are washed with water and degreased with organic solvents such as pure alcohol. The magnet specimens are placed in 5.0 - 99.0% solution of orthophosphoric acid, H_3PO_4 , or nitric acid, HNO_3 , and water for about 0.5 - 20 minutes. The NdFeB magnets are then washed in water and permitted to

dry which may be further assisted by compressed air. The magnets are thereafter subjected to high temperature thermal conditioning in accordance with the present invention at approximately 500°C-1000°C for approximately 10 to 120 minutes in a controlled atmosphere environment. The components of this controlled atmosphere are listed in TABLE 3 according to percentage by

5 volume:

TABLE 3

	<u>Component</u>	<u>Composition, vol.-%</u>
	hydrogen	0.001-0.00001
	oxygen	0.0001-21.0
10	nitrogen	0.0005-78.0
	carbon monoxide	0.0001-0.003
	carbon dioxide	0.0001-0.03
	hydrocarbons	0.0001-0.001
	water vapors	0.0005-0.05
15	helium or argon	the remaining portion of 100%

The pressure conditions in this controlled atmosphere is set at an initial pressure of approximately 1100 mm Hg and is reduced to approximately 1.0×10^{-6} mm Hg. It should be noted that in order to improve the moistening capabilities of the magnet surfaces with the

20 orthophosphoric acid solution, a surface-active substance such as olein acid may be added to the solution in various amounts ranging from approximately 0.1-5.0% by volume. Accordingly, as a result of the aforementioned process, a thin, dense and strong passivating film is formed on the surfaces of these rare earth magnets that protect them from corrosion. As explained above, this protective layer may contain stable oxides, phosphoric compounds of the elements, or other

25.

products derived from the magnet material. The precise structure and composition of the protective layer phases may of course be determined by roentgen and microroentgenospectral analytical methods, or by other accepted procedures.

The rare earth magnet and the heat passivation process described herein show 15-30% improvement of intrinsic coercive force after the thermal procedure.

While the present invention has been described with reference to the aforementioned applications, this description of the preferred embodiments and methods is not meant to be construed in a limiting sense. It shall be understood that all aspects of the present invention are not limited to the specific depictions, configurations or relative proportions set forth herein which depend upon a variety of testing conditions and variables including changes in temperature, pressure and time of exposure to thermal treatment, and may be determined through additional analysis and evaluation. Various modifications in form and detail of the various embodiments of the disclosed invention, as well as other variations of the present invention, will be apparent to a person skilled in the art upon reference to the present disclosure. It is therefore contemplated that the appended claims shall cover any such modifications or variations of the described embodiments as falling within the true spirit and scope of the present invention.

WHAT IS CLAIMED IS:

- 1 1. A rare earth based permanent magnet having a corrosion resistant surface
2 comprising:
3 a magnetic body having an external surface formed from at least one rare earth metal
4 alloy; and
5 a high temperature passivated layer substantially surrounding the external surface of the
6 magnetic body that is resistant to corrosion.
- 1 2. The rare earth magnet as recited in claim 1 wherein the magnetic
2 body is formed from a metallic alloy having a chemical composition with
3 atomic percentages consisting of 30 to 35% of neodymium, 1.0 to 1.5% of
4 dysprosium, 0.1 to 5% of cobalt, 0.75 to 1.5% of aluminum, 0.1 to 1.0% of titanium, 1.15 to
5 1.30% of boron, 0-0.1% of Uranium and a remaining percentage of iron.
- 1 3. The rare earth magnet as recited in claim 2 wherein the alloy is melted in a
2 neodymium medium.
- 1 4. The rare earth magnet as recited in claim 1 wherein the magnetic body is formed
2 from a metallic alloy having a chemical composition with atomic percentages consisting of 29 to
3 34% of neodymium, 1.15 to 1.35% of dysprosium, 0.4 to 0.8% of aluminum, 0.75 to 2.35% of
4 titanium, 1.17% of boron, 2.0 to 3.0% of cobalt, 0-0.1% Uranium and a remaining percentage of
5 iron.
- 1 5. The rare earth magnet as recited in claim 4 wherein the alloy is melted in a

2 neodymium medium.

1 6. The rare earth magnet as recited in claim 5 wherein the alloy further includes
2 additions of dysprosium, neodymium and boron melted in a medium of approximately 30.0% of
3 neodymium, 1.0% of boron, and a remaining percentage of iron.

1 7. The rare earth magnet as recited in claim 1 wherein the magnetic body is formed by
2 wet forming and milling in an organic liquid.

1 8. The rare earth magnet as recited in claim 7 wherein the organic liquid is selected
2 from the group consisting of C_2H_5OH , $C_6H_5CH_3$ and $CCl_2F-CCIF_2(CH_3)_2CHOH$.

1 9. The rare earth magnet as recited in claim 1 wherein the magnetic body is a
2 neodymium iron boron magnet, and wherein the high temperature passivated layer includes at
3 least two phases.

1 10. The rare earth magnet as recited in claim 9 wherein a first phase of the high
2 temperature passivated layer has a chemical composition with relative percentages by weight of
3 at least 84.1% of neodymium, 1.8% of iron, 0.11% of cobalt, 0.23% of aluminum, 0.088% of
4 silicon, and 0.21% of magnesium, and a second phase of the high temperature passivated layer
5 has a chemical composition with relative percentages by weight of at least 78.8% of neodymium,
6 1.8% of iron, 0.17% of cobalt, 0.004% of titanium and 0.10% of aluminum.

1 11. A method for forming a corrosion resistant rare earth magnet comprising the

2 following steps:

3 providing a rare earth magnet;

4 heating the rare earth magnet to a temperature in the range of 500 to 1000°C in a pressure

5 controlled environment; and

6 cooling the rare earth magnet to room temperature.

1 12. The method as recited in claim 11 wherein the surfaces of the magnets are initially
2 cleaned.

1 13. The method as recited in claim 12 wherein the surfaces of the magnets are degreased
2 through rinsing with an organic solvent and pickled in an acid solution.

1 14. The method of claim 13 wherein the acid solution is prepared from an acid selected
2 from the following group consisting of HNO₃, H₃PO₄ and HF.

1 15. The method of claim 13 wherein the concentration of the acid solution ranges from
2 approximately 0.001 to 100 percent by volume.

1 16. The method of claim 13 wherein the magnets are pickled in an acid solution from
2 approximately 0.5 to 25 minutes.

1 17. The method of claim 11 wherein the pressure in the vacuum environment ranges
2 from approximately 760 to 1.0×10^{-6} mm Hg.

1 18. The method of claim 11 wherein the pressure in the vacuum environment ranges
2 from approximately 8.0×10^{-4} to 9.0×10^{-4} mm Hg.

1 19. The method of claim 13 wherein the magnets are pickled in a solution of 2.5% by
2 volume of H_3PO_4 for approximately 2 minutes.

1 20. The method of claim 11 wherein the magnets are heated for approximately 30 to 120
2 minutes.

1 21. The method of claim 11 wherein the pressure in the vacuum environment is
2 controlled in a first phase and a second phase.

1 22. The method of claim 21 wherein during the first phase, the pressure in the vacuum
2 environment ranges from approximately 1.0×10^{-4} to 1.0×10^{-6} mm Hg.

1 23. The method of claim 21 wherein during the second phase, the pressure in the
2 vacuum environment ranges from approximately 1.0×10^{-2} to 1.0×10^{-4} mm Hg.

1 24. The method of claim 11 wherein the duration of the cooling process ranges from 5
2 to 30 minutes.

1 25. The method of claim 11 wherein the cooling process occurs under pressure
2 ranging from approximately 1.0×10^{-4} to 1.0×10^{-6} mm Hg.

1 26. The method of claim 11 further comprising the step of immersing the cooled
2 magnet into a polymer solution.

1 27. A method for passivating a neodymium iron boron magnet comprising the following
2 steps of:

3 providing a neodymium iron boron magnet;

4 pickling the magnet in an acid solution for approximately 0.5 to 20 minutes;

5 rinsing the magnet;

6 drying the magnet; and

7 subjecting the magnet to high temperature thermal conditioning at a selected temperature
8 ranging from approximately 500°C - 1000°C for approximately 10 to 120 minutes in a controlled
9 atmosphere environment.

1 28. The method of claim 27 wherein the pressure conditions in the controlled
2 atmosphere is regulated at an initial pressure of approximately 1100 mm Hg down to
3 approximately 1.0×10^{-6} mm Hg.

1 29. The method of claim 27 wherein the controlled atmosphere contains air.

1 30. The method of claim 28 wherein the components of the controlled atmosphere
2 according to volume percentage is approximately 0.001 - 0.000015 of hydrogen, 0.0001 - 21.0%
3 of oxygen, 0.0005 - 78.0 of nitrogen, 0.0001 - 0.003% of carbon monoxide, 0.0001 - 0.03% of
4 carbon dioxide, 0.0001 - 0.001% of carbohydrates, 0.0005 - 0.05% of water vapor, and a
5 remaining portion containing noble gases.

1 31. The method of claim 27 wherein the acid solution is an approximately 5.0 - 99.0%
2 solution of orthophosphoric acid.

1 32. The method of claim 27 wherein the acid solution is an approximately 5.0 - 99.0%
2 solution of nitric acid.

1 33. The method of claim 27 wherein a surface active substance is added to the acid
2 solution ranging from approximately 0.1 - 5.0% by volume.

1 34. The method of claim 27 wherein the high temperature passivation of the magnet is
2 carried out in an electric vacuum resistance furnace.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/14468

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B32B 15/00; H01F 01/00; C23G 01/02; C23F 15/00

US CL : 428/681; 148/100

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/681, 692, 693; 148/100, 101, 121, 122, 300, 301, 306; 427/127, 128, 129, 130, 132, 372.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	EP 0571002 A (UEDA ET AL) 24 November 1993, Abstract; page 7, lines 1-37; page 12, line 20 through page 13, line 9; page 14, line 1 through page 15, line 16; Table 2; Claims 1-19; and Figures 6-8.	1-12, 17 ---- 13-16, 18-34
X ---- Y	US 5,122,203 A (BOGATIN) 16 June 1992, column 2, line 30 through column 3, line 68; column 8, line 1 through column 10, line 13; and column 12, line 63 through column 13, line 3.	1-12, 17 ---- 13-16, 18-34
X ---- Y	US 5,282,904 A (KIM ET AL) 1 February 1994, Abstract; column 2, lines 49-68; column 3, line 40 through column 4, line 54; column 7, line 38 through column 9, line 54; and column 11, line 14 through column 12, line 59.	1-12, 17 ---- 13-16, 18-34

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

08 SEPTEMBER 1998

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/14468

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 5,173,206 A (DICKENS ET AL) 22 December 1992, Abstract; column 2, lines 35-68; column 4, line 22 through column 7, line 11; column 8, line 9 through column 9, line 9; column 9, line 38 through column 10, line 38; column 17, line 5 through column 18, line 5; and column 41, lines 1-34.	1-12, 17 ---- 13-16, 20, 27, 34
X ---- Y	US 5,470,400 A (BOGATIN ET AL) 28 November 1995, Abstract; column 2, line 61 through column 4, line 4; column 5, line 22 through column 7, line 11; column 8, line 1 through column 10, line 31; column 11, line 10 through column 14, line 53; and Claims 1-5.	1-12, 17, 20, 27, 29, 34 ---- 13-16, 18, 19, 21-26, 28, 30-33